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SURFACE QUALITY OF THE NI-TIO, COMPOSITE COATINGS PRODUCED BY ELECTROPLATING

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Abstract

Composite nickel coatings on a brass substrate were produced from suspensions consisted of a conventional nickel sulphate bath and fine TiO₂ particles ($d_p < 0.35 \ \mu m$). Characterization of coatings surface was performed by using optical and SEM micrographs, by EDS analysis and by determining the surface roughness parameters. Metallographic analysis has also been done in order to get an insight about particles distribution throughout the thickness of the coating layer. Presence of TiO₂ particles in electrodeposited metal affected the surface morphology. Particles were embedded as smaller or bigger agglomerates within the coatings, as well as the individual particles. Metallographic analysis showed uniform distribution of particles and their agglomerates within the coating. Surface roughness parameters of the composites have had up to 35 times higher values than the ones of the pure nickel coatings. Roughness maxima appeared at the concentration of particles between 10 and 20 g dm⁻³. Then it drops down and remains constant for concentrations > 40 gdm⁻³. SEM micrographs showed irregularities like single-nodule, or beads of nodules on the surface. Relationship between surface roughness and current density has not been noted.

Key words: Nickel electroplating; TiO, particles; Composite coatings; Surface roughness; Surface profilograms.

1. Introduction

Composite electrolytic coatings comprise a metal matrix into which fine inert, semi-conductive or conductive particles are incorporated from a plating bath containing corresponding metal ions and fine particles suspended in it. Particles incorporated into metal matrix change its mechanical, electric, magnetic, tribological, catalytic or optical properties. Physical properties of the composite coatings strongly depend on the particles nature as well as on the embedment quantity into the coating. Hard particles contribute to the composite coating hardness and friction properties, while soft particles will give less hard - "softer" coatings [1-4]. Inert particles will improve mechanical properties and corrosion resistance [1,3,5-7], while particles having catalytic properties, associated with metal matrix, having similar catalytic effect, lead to an enhanced catalytic feature of the composite coatings [8,9]. Regardless of the particles nature, composite coatings have as a rule an increased surface roughness [2,3].

Tanking to emerging of nano-sized dispersive materials, a special attention has been paid in '90s, to the electrochemical production and characterisation of the composite coatings. The intention was to produce composite coatings having, besides enhanced mechanical and anti-corrosive features, a beneficial either electric, magnetic, catalytic, or optical quality [2,5,6,10].

Copper [1,7,11] and nickel [2-6,8,9,12-22], as well as their alloys, have been frequently used as a metal matrix in composite coatings production and characterization. Due to its exceptional metallic properties, nickel has particularly been used for a long time in metal finishing processes to protect and improve surface of various metallic and plastic products. For these reasons, nickel has been most frequently used as a good matrix for production and characterization of composite coatings. Different combinations of fine particles and nickel have been recently used as a model-system in the studies, as: Ni-SiC [3,19,21]; Ni-Al₂O₃ [3,20,22]; Ni-La₂O₃ [5]; Ni-ZrO₂ [15]; Ni-C (graphite) [17]; Ni-PTFE [18]. An

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increased attention has been paid to producing and further characterization of nickel composite coatings with TiO₂ sub-micron or nano-sized particles [2,3,5,8-10,13,14,16]. The investigations have had a fundamental but also an applicative nature, particularly in photo-electrochemistry, as well as in photo-catalytic processes [7,8-10,12]. Simultaneous embedment of TiO₂ and RuO₂ into Ni matrix [9], as well as Fe₂O₃ and TiO₂ into Ni-P alloy and the catalytic effect of such composites in water electrolysis and hydrogen production was the main subject of the investigations published recently [10].

Not too much attention has been paid yet to the surface roughness of these composites. Because of that, the aim of this study was to produce composite coatings from the nickel bath, in which TiO_2 fine particles were suspended, and to carry out characterisation of their surface. Influence of the concentration of particles in the bath and the operating current density on the obtained composites quality will be monitored. Pure nickel coatings, electroplated from the nickel bath alone, under the same other experimental conditions, will serve for comparison of the surface quality between them and the corresponding composites.

2. Experimental

2.1 Materials and Methods

2.1.1 Cell and electrodes

Production of the nickel composite coatings by the electroplating was carried out by using the nickel sulphate electrolyte in which submicron-sized TiO₂ particles were suspended. The experiments were performed in a laboratory glass cell (volume 600 cm³), equipped with both magnetic bar stirrer and a heater. Samples (15 x 17x 1 mm), cut from brass sheet, served as cathodes while the anodes were cut from pure, cold rolled nickel plates casted and rolled in the Metallurgical Engineering Department of the Technical Faculty Bor. In order to obtain better current distribution, the anodes have had approximately 10 times larger geometric surface than the cathode.

2.1.2 Chemicals

 $\rm NiSO_4$ commercial bath (producer's mark Ni-EX) was commissioned by the Metal Salt Factory, RTB Bor, . The nickel bath was delivered in the form of "ready to use" solution, meaning that beside Ni²⁺ ions of a given concentration, it contains corresponding concentration of Cl⁻ and SO₄ ²⁻ anions, as well as all the other additives for producing bright and ductile nickel electrocoatings. The pH was also adjusted by the provider, so that no additional adjustment was necessary. Nickel bath chemical composition is given in Table 1.

 Table 1. Chemical composition of the nickel bath used in the electroplating experiments

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Ni ²⁺	SO4 ²⁻	Cl-	H ₃ BO ₃	pН	Additives
75 gdm ⁻³	70 gdm-3	40 gdm ⁻³	45 gdm ⁻³	4.5-5.5	Not specified

For the brass surface degreasing and deoxidizing, prior the electroplating, the solutions of the commercial mark Hemobeland Homb, were provided from the same producer, providing us the bath for nickelling.

Titania nanoparticles, producer's trade-mark: RC8/1, No 145, was provided by "Cinkarna". The size of particles was in a range of 200 to 350 nm. Having a tendency towards agglomeration due to their high surface energy [13], a certain, fraction of aggregates, with a size < 4 μ m, always exists in the TiO₂ powder. This fact, associated with titania wettability, requested longer time of bath stirring, prior to switching the cell on, in order to make as much as possible homogeneous suspension with a minimum agglomerates in it.

2.1.3 Equipment for the electroplating and characterization of produced coatings

Magnetic stirrer, equipped with a heater was used to form the bath suspension and to warm it up, as well as to keep particles fully suspended during the electroplating process. All the electroplating experiments were carried out at 55°C, recommended by the producer as an optimum working temperature. Potentiostat-Galvanostat - 555B "Amel", served as a direct current (DC) supplier. The operating current and the cell voltage were monitored by ammeter and voltmeter, while the pH was periodically controlled by pH-meter.

The following methods and corresponding equipment were used for characterization of the produced nickel electrocoatings:

- Scanning electron microscopy (SEM), with Energy-dispersive X-ray spectroscopy (EDS) (SEM, JEOL JSM-6460);
- Optical microscopy (OLIMPUS BX51 Metallurgical Microscope);
- Metallographic analysis (EPITYP 2 Metallographic Microscope – magnification up to 500 times);
- Photos were taken by using digital camera SONY DSC-W30;
- Surface roughness (PERTHOMETER S8P Mahr GmbH, Germany).

2.2 Procedure of composite coatings production and characterization

In order to degrease and deoxidize the surface to



be plated, the cathodes were pretreated by using corresponding solutions for degreasing and deoxidizing in accordance to "the instruction for use", provided by the supplier. The prepared cathode was fixed between two anodes, making a stable side-byside electrodes configuration. Inter-electrode distance of 50 mm kept constant in all experiments.

The electrolyte suspension, of desired concentration of particles, was prepared by dispersing a previously weighed amount of titania particles in the nickel bath (V= 500 cm³) while stirring at 400 rpm, in order to break as much as possible the existing agglomerates of TiO₂ particles and to keep them in suspension. Suspension was simultaneously stirred and warmed up until reaching of the operating temperature of 55 °C.

The electrodes arrangement (cathode between two anodes) was immersed into the suspension and fastened to avoid any twisting or oscillating during the electroplating. Electrodeposition was carried out galvanostatically for 70 minutes in all experiments. In order to compare a difference between the composite and pure nickel coatings, a series of electroplating experiments were carried out from the nickel bath alone but keeping the same other experimental conditions, i.e. the current density, stirring rate, temperature and electroplating time. Pretreatment of the electrodes and posttreatment and the produced composites characterization one can find described in details elsewhere [25].

3. Results and discussion

3.1 Characterization of the nickel coatings produced from an empty bath

Samples of the electroplated nickel coatings from an empty bath were obtained at different current densities in the previously described way. They were characterized by taking the optical and SEM micrographs, as well as by recording the surface profilograms, for deriving the surface roughness parameters from them. The obtained results are presented in Fig. 1 and Fig. 2, while the surface roughness parameters are given in Table 2.

Very smooth coatings were produced from the empty bath as it is seen from optical, Fig 1 (a), and confirmed by the SEM micrograph taken at magnification of 10.000 times (b).

As stated above, the surface profilograms were measured on three profiles across the surface for each sample.

The results of these measurements are partly presented by two profilograms in Fig. 2, recorded for the highest and the lowest current density. Presented profilograms show small amplitudes deviations from an average value across the whole surface area of each sample, confirming its very high smoothness.

Figure 1. Optical (a) and SEM image (b) of the pure nickel coating: $I = 2 A dm^{-2}$

Profilograms, given in Fig.2, have not shown any significant difference in their shape across the whole surface area. Amplitudes of the individual roughness parameters were computed automatically from the profilograms and displayed on the screen.

Values of surface roughness parameters are presented in Table 2, for all the applied current densities.



Figure 2. Profilograms of the pure nickel coatings obtained at the lowest and highest current density

 Table 2. Surface roughness parameters of the pure nickel coatings – effect of applied current density

i, A dm ⁻²	Rmax, µm	Ra, µm	Rz, μm	Wt, µm
2	0.19	0.03	0.12	0.365
4	0.097	0.016	0.068	0.35
6	0.24	0.032	0.14	0.6
10	0.164	0.017	0.09	0.44
20	0.173	0.029	0.13	0.88

Where: Rmax is a maximum distance between two lines parallel to the mean line at distance L; Ra -



arithmetic mean of the absolute values of z(x), defined by equation: , L - linear dimension of the sample; Rz - mean height/depth of the roughness in 10 points defined as: , z_p - peaks height; z_v - valley depth; Wt- distance between the highest peak and the deepest valley on the sample linear dimension L . For more details readers can inform themselves to [23,24].

Very small values of the surface roughness parameters, presented in Table 2, show in a quantitative way a very high smoothness of coating obtained from the empty bath. This is particularly expressed by Ra, where the absolute values do not exceed 32 nm, as well as Rz, the values of which are ≤ 140 nm. Such results were expectable, as it is known that nickel possesses a feature of giving good and uniform electrocoatings onto a metal substrate. There is not any noticeable regular dependence between the applied current density and the surface roughness parameters.

3.2 Optical, SEM and EDS analysis of the composite coatings - microstructure and morphology of the composites

Optical and SEM micrographs of the composite coatings surface, obtained from nickel bath with suspended TiO_2 particles, are presented in Fig. 3. Obviously, composite coatings showed a different image in comparison to the coatings obtained from the nickel bath alone. Unlike from surface, presented by micrographs in Fig. 1, the surface of nickel composite coatings is significantly rougher, with numerous nodules, visible even at smaller magnifications, as is seen from the optical image in Fig 3 (a). This is caused by the particles embedded in the coating, what is evident from the SEM image given in Fig. 3 (b).

Besides individual TiO_2 particles, there are bigger or smaller agglomerates on the surface, contributing to an increase in the surface roughness. Size of the agglomerates varies, reaching in some cases even several microns, as is illustrated in Fig. 4.

What is seen as nodules in micrographs taken by optical microscope (See Fig.3 (a)), at higher

magnifications has a much complex structure, consisting from bigger or smaller clusters of particles, as shown in Fig. 4.



Figure 4. Detail of particles agglomerate on the surface and the size of single particles and smaller agglomerates in them: $i = 10 A dm^2$; $C_{TiO_2} = 10 g dm^2$

Metallographic analysis of the composite coating cross section showed uniform distribution of TiO_2 agglomerates through the whole coating thickness, as illustrated in Fig. 5. Such an image was expected.

At higher concentration of TiO_2 in the bath, there are certain irregularities on the surface in the form of whiskers or beads of nodules, as shown in Fig 6, formed because of the bath stirring and streamlines movement along the electrode surface [1,3,26].

Obviously, the embedded particles and nodules are not distributed uniformly over the surface. There are some parts of the surface area without nodules, while the other ones where agglomerates are ordered as beads, as a consequence of the hydrodynamic image in the electrode vicinity, what is also visible from Fig. 6.









Figure 3. Optical (a) and SEM (b) image of the nickel-TiO₂ composite: $i = 20 A dm^{-2}$; $C_{TiO_2} = 10 g dm^{-3}$







Figure 6. SEM micrographs of beads and agglomerates of TiO₂ particles on the surface of the composite coating taken at two magnifications: $i = 10 \text{ A dm}^{-2}$; $C_{\text{TiO}} = 80 \text{ g dm}^{-3}$;

Inclusions that appear on the composites surface were analysed by means of EDS and the corresponding spectra are presented in Fig. 7. On the spectrograms, for the coatings electroplated from the bath alone, only elemental nickel has been detected (a). Elemental nickel and titanium are detected in case of the composite coatings (b).

The surface roughness parameters were measured on three profiles for each sample. The obtained measurements are presented as original profilograms in Fig. 8 a - for samples obtained at the lowest and highest applied current density, as well as in Fig 8 b recorded for the lowest and highest titania concentration of particles.



Figure 7. EDS spectrograms of pure (a) and composite Ni-TiO, (b) electrocoatings

3.3 Surface roughness of the composites coatings

The intention was to illustrate a qualitative contribution of particles embedded in coating to the profilograms shape and, consequently, to the surface roughness parameters values, which are presented in Table 3.



Figure 8. Profilograms recorded for two different current densities (a: $C_{TiO} = 10 \text{ g dm}^3$), and at two different concentrations of TiO₂ in the bath (b: $i = 10 \text{ A dm}^2$)

A brief insight into Fig. 8 and Fig. 2 demonstrates a strong difference between these profilograms what was also discussed in detail elsewhere [23]. Profilograms, presented in Fig. 8, are more expressive than those in Fig. 2, having larger and sharper fluctuation of amplitudes, as a measure of the surface roughness. They have much higher peaks and much deeper valleys, compared to the profilograms recorded for the pure nickel coatings, for both changed parameters – current density and concentration of TiO₂ particles in the bath. Moreover,

Table 3. Surface roughness parameters of the compositecoatings – effect of the applied current density: $C_{Tio}=10 \text{ g dm}^{-3}$

i, A dm ⁻²	Rmax, µm	Ra, µm	Rz, μm	Wt, µm
2	2.4	0.376	1.84	2.38
4	3.1	0.367	1.75	3.03
6	0.87	0.162	0.72	2.04
10	2.14	0.32	1.5	3
20	2	0.283	1.1	2.156



frequency of fluctuations appearance and disappearance is also higher in case of profilograms relating to the composite coatings.

Contribution of the current density (better to say the electrode potential), to the surface quality was already considered, too [2,25,26]. Current density determines the deposition rate of metal ions, as well as the grain size of deposited metal. Here, it could only be pointed out that higher values of surface roughness parameters (rougher surface) were obtained at lower, as well as at higher current densities, while minimum values were achieved at 6 A dm⁻², what is connected with the minimum amount of embedded particles at this current density [2,26]. It can be said that there is no a clear functional dependence between current density and surface roughness parameters, what arises from Table 3. Comparing data from Table 2 and 3, it can be seen that surface roughness parameters are for one order of magnitude higher in case of Ni-TiO₂ composites. It means a dramatic jump in developing the real surface of composites in relation to the pure nickel coating surface.

Keeping the current density at 10 A dm⁻² and changing the concentration of TiO_2 particles in suspension, a series of coatings were produced and the surface quality was analysed in the same way as in the previous case. The effect of concentration of particles in the bath on the surface roughness parameters is presented in Table 4 and in Fig. 9 to get an insight in the roughness parameters plotted against the concentration of particles.

Table 4. Surface roughness parameters of the composite
coatings – effect of concentration of particles in the
bath: $i = 10 A dm^2$

C _{TiO2} , g dm ⁻³	Rmax, µm	Ra, µm	Rz, μm	Wt, µm
0	0.164	0.017	0.09	0.44
10	2.14	0.32	1.5	3
20	2.7	0.45	1.9	4.1
40	1.1	0.16	0.86	2.74
80	1	0.165	0.8	1.93

Surface roughness parameters increases with increasing concentration of particles in the bath to approximately 20 g dm⁻³. Going towards higher concentrations, they started suddenly decreasing, reaching approximately a constant value for concentrations ≥ 40 g dm⁻³. That could be attributed to an attrition effect of the suspended particles, acting as a polishing agent in relation to the electrode surface, removing partly already attached particles, which have not yet been firmly embedded in coating by the deposited metal. It means that higher concentrations of particles in motion have a levelling effect to the coating, leading to smoother areas on surface of the

composites and consequently to lowering of the corresponding surface roughness parameters. Besides this, higher concentrations of particles in suspension corresponds an increased appearance of the irregularities on the surface area. Though, the amount of embedded particles goes up too, with increasing the concentration [2, 25, 26].

Since every surface area is characterised by a certain roughness on a micro-scale, it would be good to see the net contribution of embedded particles to the surface roughness of the composite coatings. Defining the term "net contribution" of the particles to the surface roughness, as a difference between surface roughness parameters of composites and corresponding parameters measured for pure nickel coatings, as: Ri – Ri_o, where subscript "o" denotes roughness parameters relating to pure nickel coatings, the contribution of embedded particles to the surface roughness parameters relating to pure nickel coatings, the contribution of embedded particles to the surface roughness can be quantified, what is presented in Fig. 9.



Figure 9. Net contribution of TiO_2 concentration to the roughness parameters: $i = 10 \text{ Adm}^2$

It comes out from Fig. 9 that the concentration of particles has the largest effect to the $\text{Rmax} - \text{Rmax}_{o}$, while the lowest to $\text{Ra} - \text{Ra}_{o}$, due to very small values of Ra_{o} for the pure nickel coatings. Because of that, the net contribution of concentration of particles gives no clear effect of the embedded particles to the surface roughness of composites.

It seems as if a better approach would be to normalize roughness parameters as a ratio of corresponding roughness parameters of composites Ri and of pure nickel coating Ri_o , i.e. Ri/Ri_o . Plotting Ri/Ri_o against the concentration of particles a better insight can be achieved on that how the concentration of TiO₂ particles in suspension affects the surface roughness and how many times will be the considered roughness parameter enlarged due to the particles embedment into the coatings, what is presented in Fig. 10.

Optical images also showed that higher concentration of titania in the bath leads to a smoother areas on the composite surface, with less number of nodules and increased number of single particles or smaller clusters embedded onto the surface, but with



an increased number of irregularities, what has already been discussed before. The obtained SEM micrographs reveal the existence of rare nodules as a group of islands onto the surface. By them, nodules are smaller at the concentration of particles of 80 g dm⁻³ in the suspension.



Figure 10. Normalized roughness parameters vs. TiO_2 concentration: $i = 10 A dm^2$

Chemical analysis revealed that the fraction of titania in the coating, plotted against the concentration of particles in suspension (Fig. 11), showed a complex relationship between these two variables. There is no significant difference in the titania percentage built into the composite produced from the bath containing the lowest (10 gdm⁻³) and the highest (80 gdm⁻³) concentration of particles. In the considered case it is approximately one percent.

A big difference exists in the surface quality, particularly in its roughness. It could mean that the composites, deposited from more concentrated suspensions, contain almost the same amount of included titania as the ones produced from 8 times lower concentration. At less concentrated suspensions, the embedded titania particles are in the



Figure 11. Fraction of embedded particles in the composite vs. concentration of particles in the suspension: $i=10 \text{ Am}^2$

form of bigger or smaller nodules homogeneously distributed through and across the coating. At more concentrated suspensions, composite coatings look smoother; the embedment of particles takes place rather in the form of single particles or smaller nodules, but with more irregularities. These irregularities could be reduced by changing the way of keeping particles in suspension, as well as by changing the turbulence intensity in the bath. The question only is what kind of the surface quality is needed - to be smoother or rougher. It would depend on that where the composite coating will be applied. Namely, rougher surface means more developed surface what could particularly be beneficial in transport phenomena, as is the case of heat transfer with change of phase (in boiling or condensation phenomenon), as well as in mass transfer with fast chemical, catalytic or electrochemical reaction. In such cases, an increased surface roughness of composite coating, as well as the presence of particles on the surface, could have several engineering implications. It is well known that heat transfer with the change of phases occurs more intensively on rougher surfaces than on smoother ones. Rougher surface contributes also to the chemical/electrochemical reactions with gas evolution as a reaction product. If the embedded particles have a catalytic effect towards a chemical reaction, composite coatings will contribute in an extent, which is proportional to the surface concentration of particles [9,10].

4. Conclusions

Composite coatings of nickel and fine titania particles were produced by the electrodeposition of nickel from the commercial nickel sulphate bath, in which TiO_2 particles of sub-micron size were suspended by magnetic stirring. During the electroplating, particles were attracted to the electrode surface and incorporated into metal matrix.

Metallographic analysis of the coating crosssectional area of the cut samples has shown a uniform distribution of embedded TiO_2 particles and their agglomerates throughout the thickness of the coating.

SEM and metallographic micrographs have also shown that particles are embedded in the metal matrix in the form of smaller or bigger agglomerates but much less as single particles.

Optical micrographs, even at smaller magnifications detected numerous nodules on the composite coatings surface. The nodules are more expressed at lower current densities and particularly at lower concentrations of titania in the suspension.

The surface roughness was investigated by means of profilograms recorded across the coating surface and quantified by surface roughness parameters



derived from them. The presence of embedded particles in composite coatings strongly affects the surface quality of composites, making it rougher 15 to 30 times than the surface obtained by electroplating from nickel bath alone. Concentration of particles in suspension strongly affects the surface roughness. Surface roughness parameters sharply increase with an increase of the concentration of particles in the suspension. At concentrations > 20 gdm⁻³ surface roughness decreases, reaching almost a constant value for concentrations \geq 40 gdm⁻³, which was attributed to an attrition effect of suspended particles moving over the electrode surface.

Composites produced from more concentrated suspensions have an increased number of irregularities in the form of whiskers or beads of nodules as a consequence of hydrodynamic occurrences in the bath close to the electrode surface. It could be concluded that higher concentration of particles in suspension has a polishing effect leading to a smoother and brighter composite coating.

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